



## **APPLICATION FOR UNITED STATES PATENT**

**Inventor(s):** CORR, Stuart

**Invention:** LUBRICANTS

Cushman, Darby & Cushman  
1100 New York Avenue N.W.  
Ninth Floor  
Washington, D.C. 20005-  
Attorneys  
Telephone: 861-3000

## **SPECIFICATION**

# 957080  
A 1008/976658  
FBS



107  
13

LUBRICANTS

5

The present invention relates generally to lubricants and more particularly to working fluid compositions contained in heat transfer devices which comprise the lubricant and a heat transfer fluid.

10

15

20

Heat transfer devices of the mechanical compression type such as those used in refrigerators, freezers, heat pumps and automobile air conditioning systems are well known. In such devices a heat transfer fluid of a suitable boiling point evaporates at low pressure taking heat from a surrounding zone. The resulting vapour is then compressed and passes to a condenser where it condenses and gives off heat to a second zone. The condensate is then returned through an expansion valve to the evaporator so completing the cycle. The mechanical energy required for compressing the vapour and pumping the fluid is provided by, for example, an electric motor or an internal combustion engine.

25

30

35

The heat transfer fluids used in these heat transfer devices include chlorine containing fluoroalkanes such as dichlorodifluoromethane (R-12), chlorodifluoromethane (R-22) and mixtures thereof with, for example, fluoroalkanes such as 1,1-difluoroethane (R-152a). However, such chlorine containing fluoroalkanes have been implicated in the destruction of the ozone layer and as a result the use and production thereof is to be severely limited by international agreement. The use of certain fluoroalkanes and hydrofluoroalkanes in place of the chlorine containing fluoroalkanes has been proposed. The fluoroalkanes and hydrofluoroalkanes of particular interest are those compounds which have comparable

5 boiling points and other thermal properties to the chlorine containing fluoroalkanes which they are replacing, but which are also less damaging or benign to the ozone layer. Thus, R-12 is generally being replaced by a new refrigerant, 1,1,1,2-tetrafluoroethane (R-134a).

10 Hitherto, heat transfer devices have tended to use mineral oils as lubricants. The good solubility of chlorine containing fluoroalkanes with mineral oils allows the mineral oil to circulate around the heat transfer device together with the chlorine containing fluoroalkane, and this in turn ensures proper  
15 lubrication of the compressor. Unfortunately, however, the replacement fluoroalkane and hydrofluoroalkane heat transfer fluids such as R-134a have different solubility characteristics to the chlorine containing fluoroalkanes presently in use and tend to be  
20 insufficiently soluble in mineral oils to allow the latter to be used as lubricants. Consequently, numerous alternative lubricants such as polyoxyalkylene glycols terminating in hydroxyl and other groups, esters of polyols with mono- and polyfunctional acids, and halo substituted esters and ethers have been proposed as  
25 lubricants for use with the replacement heat transfer fluids.

30 Unfortunately, R-134a cannot be used as a direct replacement for certain of the refrigerants which are presently in use such as R-22 and R-502 (an azeotropic mixture of R-22 and chloropentafluoroethane R-115) since it does not possess comparable boiling  
characteristics and thermal properties. It has thus been proposed that existing refrigerants such as R-22  
35 and R-502 be replaced by refrigerant mixtures comprising two or more refrigerants selected from the

5 fluoroalkanes and hydrofluoroalkanes. Particular  
mention may be made of binary mixtures of refrigerants  
such as R-134a and difluoromethane (R-32) or R-32 and  
pentafluoroethane (R-125). Unfortunately, these  
refrigerant mixtures are also not sufficiently soluble  
10 in mineral oils to allow the latter to be used as  
lubricants. Moreover, the miscibility and solubility of  
an alternative lubricant with one component of the  
mixture, for example with R-134a, does not mean that  
such a lubricant will also be miscible and soluble with  
the refrigerant mixture itself. In consequence, the  
15 development of a lubricant which exhibits acceptable  
lubricating properties in a heat transfer device  
utilising a refrigerant mixture presents a very real  
problem.

It has now been found that if a prospective  
20 lubricant is at least partially soluble in each  
component of the refrigerant mixture then it will be at  
least partially soluble in the refrigerant mixture  
itself, thereby enabling its use as a lubricant with  
that mixture. Such a lubricant may provide an  
acceptable lubricating action even if it is immiscible  
25 with one or more of the components of the refrigerant  
mixture or with the refrigerant mixture itself.

According to the present invention there is  
provided a working fluid composition comprising  
(A) a heat transfer fluid comprising a mixture of at  
30 least two compounds selected from the group consisting  
of hydrofluoroalkanes and fluoroalkanes; and  
(B) sufficient to provide lubrication of a lubricant  
which is at least partially soluble in each component  
of the heat transfer fluid.

35 The heat transfer fluid may comprise two, three or  
more components. Preferred hydrofluoroalkanes and

5 fluoroalkanes are selected from the group consisting of difluoromethane (R-32), 1,1,2,2-tetrafluoroethane (R-134), 1,1,1,2-tetrafluoroethane (R-134a), pentafluoroethane (R-125), 1,1-difluoroethane (R-152a), 1,1,1-trifluoroethane (R-143a) and 1,1,2-trifluoroethane (R-143).

10 One suitable heat transfer fluid comprises a mixture of R-32 and R-125. Such a mixture may comprise equal proportions of each component on a weight basis.

15 The present invention is particularly concerned with the provision of a working fluid composition which provides a useful replacement for the working fluids presently in use which comprise R-22 or R-502 as the refrigerant and a mineral oil lubricant. A particularly desirable working fluid composition in this respect is one which comprises

20 (A) a heat transfer fluid comprising a mixture of:

- (1) tetrafluoroethane;
- (2) at least one hydrofluoroalkane selected from the group consisting of difluoromethane (R-32) and 1,1,1-trifluoroethane (R-143a); and optionally
- (3) pentafluoroethane (R-125); and

25 (B) sufficient to provide lubrication of a lubricant which is at least partially soluble in each component of the heat transfer fluid.

30 The tetrafluoroethane may be 1,1,1,2-tetrafluoroethane (R-134a) or 1,1,2,2-tetrafluoroethane (R-134) or a mixture of these two isomers. Preferably, however, the tetrafluoroethane is a single isomer, and more preferably is R-134a.

35 Although the heat transfer fluid may comprise more than three components, it is preferably a binary or ternary mixture. The mixture may be an azeotrope or near-azeotrope, but will normally be zeotropic.

5

5 In one preferred embodiment of the present invention, the heat transfer fluid is a binary mixture consisting essentially of R-134a and R-32. Such a mixture provides a particularly suitable replacement for the R-22 refrigerant which has been used hitherto in commercial refrigeration systems and related heat transfer devices. Preferably, such a mixture comprises 10 from 45 to 75 % by weight, more preferably from 65 to 75 % by weight of R-134a and from 25 to 55 % by weight, more preferably from 25 to 35 % by weight of R-32. A particularly preferred binary mixture comprises about 15 70 % by weight of R-134a and about 30 % by weight of R-32.

In a further preferred embodiment of the present invention, the heat transfer fluid comprises a ternary or higher mixture of:

- 20 (1) R-134a or R-134;  
(2) at least one hydrofluoroalkane selected from the group consisting of R-32 and R-143a; and optionally  
(3) R-125.

25 Such a heat transfer fluid provides a suitable replacement for the R-22 and R-502 refrigerants which have been used hitherto in commercial refrigeration systems and related heat transfer devices.

Particularly suitable ternary heat transfer fluids may be selected from:

- 30 (a) R-134a + R-32 + R-143a;  
(b) R-134 + R-32 + R-143a;  
(c) R-134a + R-32 + R-125;  
(d) R-134 + R-32 + R-125;  
(e) R-134a + R-143a + R-125; and  
(f) R-134 + R-143a + R-125.

35 A particularly preferred heat transfer fluid comprises a mixture of:

- 5 (1) R-134a or R-134, especially R-134a;  
(2) R-32 or R-143a, especially R-32; and  
(3) R-125.

Such heat transfer fluids provide a particularly suitable replacement for R-22 and R-502.

10 One particularly preferred ternary heat transfer fluid for replacing R-22 is a mixture consisting of:

- (1) 55 to 65 % by weight, particularly about 60 % by weight of R-134a;  
(2) 25 to 35 % by weight, particularly about 30 % by weight of R-32; and  
15 (3) 5 to 15 % by weight, particularly about 10 % by weight of R-125.

Another particularly preferred ternary heat transfer fluid for replacing R-22 is a mixture consisting of:

- 20 (1) 25 to 35 % by weight, particularly about 30 % by weight of R-134a;  
(2) 45 to 55 % by weight, particularly about 50 % by weight of R-32; and  
(3) 15 to 25 % by weight, particularly about 20 % by weight of R-125.

25 One particularly preferred ternary heat transfer fluid for replacing R-502 is a mixture consisting of:

- (1) 45 to 55 % by weight, particularly about 50 % by weight of R-134a;  
30 (2) 25 to 35 % by weight, particularly about 30 % by weight of R-32; and  
(3) 15 to 25 % by weight, particularly about 20 % by weight of R-125.

35 Another particularly preferred ternary heat transfer fluid for replacing R-502 is a mixture consisting of:

(1) 45 to 55 % by weight, particularly about 50 %  
by weight of R-134a;

(2) 35 to 45 % by weight, particularly about 40 %  
by weight of R-32; and

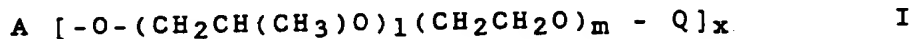
(3) 5 to 15 % by weight, particularly about 10 %  
by weight of R-125.

All the percentages by weight quoted above are  
based on the total weight of the ternary heat transfer  
fluid.

Suitable lubricants may be selected from those  
currently used with R-134a provided that the  
requirement of partial solubility is met.

Lubricants satisfying the requirement of partial  
solubility may, in particular, be selected from the  
class known in the art as polyoxyalkylene glycols.  
Suitable polyoxyalkylene glycol lubricants include  
hydroxyl group initiated polyoxyalkylene glycols, e.g.  
ethylene and/or propylene oxide oligomers/polymers  
initiated on mono- or polyhydric alcohols such as  
methanol, butanol, pentaerythritol and glycerol. Such  
polyoxyalkylene glycols may also be end-capped with  
suitable terminal groups such as alkyl, e.g. methyl  
groups.

A preferred polyoxyalkylene glycol lubricant is  
one having an average molecular weight in the range of  
from about 150 to about 3000 and comprising one or more  
compounds of general formula:



wherein



5 A is the residue remaining after removing the hydroxyl groups from a hydroxyl containing organic compound;

Q represents an optionally substituted alkyl, aralkyl or aryl group;

1 and m are independently 0 or an integer provided that at least one of 1 or m is an integer; and

30 x is an integer.

15 The polyoxyalkylene glycol lubricant may be prepared using conventional techniques. Such techniques are well known to those skilled in the art. Thus, in one method a hydroxyl containing organic compound such as an alcohol is reacted with ethylene oxide and/or propylene oxide to form an ethylene oxide and/or propylene oxide oligomer/polymer containing terminal hydroxyl groups which is subsequently etherified to give a polyoxyalkylene glycol of Formula I. The  
20 polyoxyalkylene glycol lubricant which is finally formed will not usually consist of a single compound of Formula I, but will usually comprise a mixture of such compounds which vary from one another in respect of the degree of polymerisation, i.e. the number of ethylene  
25 and/or propylene oxide residues. Moreover, a mixture of alcohols and/or phenols may be used as initiators in the formation of the polyoxyalkylene glycol lubricant, and a mixture of etherifying agents which provide different Q groups may also be used. The molecular  
30 weight of a polyoxyalkylene glycol lubricant comprising a mixture of compounds of Formula I will represent the average molecular weight of all the compounds present, so that a given lubricant may contain specific polyoxyalkylene glycols which have a molecular weight  
35 outside the range quoted above, providing that the

average molecular weight of all the compounds is within that range.

The moiety A in the polyoxyalkylene glycol of Formula I is the residue remaining after removing the hydroxyl groups from a hydroxyl containing organic compound. Such compounds include the mono- and polyhydric alcohols and phenols. Where the hydroxyl containing organic compound which is used as an initiator in the formation of the polyoxyalkylene glycol is a monohydric alcohol or phenol, A is preferably a hydrocarbyl group and more preferably is an alkyl, aryl, alkaryl or aralkyl group, especially alkyl. Suitable alkyl groups for A may be selected from the straight chain (linear), branched or cyclic alkyl groups. Preferably, A is a C<sub>1-12</sub>, particularly a C<sub>1-10</sub> and especially a C<sub>1-6</sub> alkyl group. Specific examples of alkyl groups include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, the various pentyl groups, the various hexyl groups, cyclopentyl, cyclohexyl and the like. Particularly preferred alkyl groups for A are the C<sub>1-12</sub>, particularly the C<sub>1-10</sub> and especially the C<sub>1-6</sub> straight chain alkyl groups, examples of which have been listed above. An especially preferred alkyl group for A is methyl or n-butyl.

Other suitable hydrocarbyl groups for A are those which remain after removing a hydroxyl group(s) from benzyl alcohol and phenols such as phenol, cresol, nonylphenol, resorcinol and bisphenol A.

Where a polyhydric alcohol is used in the formation of the polyoxyalkylene glycol, A is preferably a hydrocarbon radical. Suitable hydrocarbon radicals for A are those which remain after removing the hydroxyl groups from polyhydric alcohols such as

5 ethylene glycol, propylene glycol, 1,4-butanediol,  
1,6-hexanediol, diethylene glycol, dipropylene glycol,  
cyclohexane dimethanol, glycerol, 1,2,6-hexane triol,  
trimethylolpropane, pentaerythritol, dipentaerythritol  
and sorbitol. A particularly preferred hydrocarbon  
radical for A is that remaining after removing the  
hydroxyl groups from glycerol.

10 The moiety Q in the polyoxyalkylene glycol of  
Formula I is an optionally substituted alkyl, aralkyl  
or aryl group. A preferred optionally substituted  
aralkyl group for Q is an optionally substituted benzyl  
15 group. Preferred optionally substituted aryl groups for  
Q include phenyl and alkyl substituted phenyl groups.  
Preferably, Q is an optionally substituted, for example  
halogen substituted, alkyl group, particularly an  
optionally substituted C<sub>1-12</sub> alkyl group and more  
20 particularly an optionally substituted C<sub>1-4</sub> alkyl  
group. Suitable alkyl groups for Q may be selected from  
the straight chain (linear), branched or cyclic alkyl  
groups, especially the linear alkyl groups. Although  
the alkyl groups for Q are described as being  
25 optionally substituted, they are preferably  
unsubstituted. Accordingly, particularly preferred  
alkyl groups for Q are selected from methyl, ethyl,  
propyl, isopropyl and the various butyl groups. An  
especially preferred alkyl group for Q is methyl.

30 The polyoxyalkylene glycol of Formula I may be a  
polyoxyethylene glycol, a polyoxypropylene glycol or a  
poly(oxyethylene/oxypropylene) glycol. In the latter  
case, the ethylene and propylene oxide residues may be  
arranged randomly or in blocks along the polymer chain.  
Preferred polyoxyalkylene glycols are the  
35 polyoxypropylene glycols and the  
poly(oxyethylene/oxypropylene) glycols.

||

5 Particularly preferred lubricants for use in the  
working fluid compositions of the invention are those  
selected from the class known as neopentyl polyol  
esters due, inter alia, to their generally high level  
of thermal stability. Suitable neopentyl polyol esters  
include the esters of pentaerythritol,  
10 polypentaerythritols such as di- and  
tripentaerythritol, trimethylol alkanes such as  
trimethylol ethane and trimethylol propane, and  
neopentyl glycol. Such esters may be formed with linear  
and/or branched aliphatic carboxylic acids, such as  
15 linear and/or branched alkanolic acids, or esterifiable  
derivatives thereof. A minor proportion of an aliphatic  
polycarboxylic acid, e.g. an aliphatic dicarboxylic  
acid, or an esterifiable derivative thereof may also be  
used in the synthesis of the ester lubricant in order  
20 to increase the viscosity thereof. However, where such  
an aliphatic polycarboxylic acid (or esterifiable  
derivative thereof) is employed in the synthesis, it  
will preferably constitute no more than 30 mole %, more  
preferably no more than 10 mole % of the total amount  
25 of carboxylic acids (or esterifiable derivatives  
thereof) used in the synthesis. Usually, the amount of  
the carboxylic acid(s) (or esterifiable derivative  
thereof) which is used in the synthesis will be  
sufficient to esterify all of the hydroxyl groups  
30 contained in the polyol, but in certain circumstances  
residual hydroxyl functionality may be acceptable.

A preferred neopentyl polyol ester lubricant is  
one comprising one or more compounds of general  
formula:



wherein

5 R is the hydrocarbon radical remaining after removing the hydroxyl groups from pentaerythritol, dipentaerythritol, tripentaerythritol, trimethylol ethane, trimethylol propane or neopentyl glycol, or the hydroxyl containing hydrocarbon radical remaining after removing a proportion of the hydroxyl groups from  
10 pentaerythritol, dipentaerythritol, tripentaerythritol, trimethylol ethane, trimethylol propane or neopentyl glycol;

each  $R^1$  is, independently, H, a straight chain (linear) aliphatic hydrocarbyl group, a branched  
15 aliphatic hydrocarbyl group, or an aliphatic hydrocarbyl group (linear or branched) containing a carboxylic acid or carboxylic acid ester substituent, provided that at least one  $R^1$  group is a linear aliphatic hydrocarbyl group or a branched aliphatic  
20 hydrocarbyl group; and

n is an integer.

The aliphatic hydrocarbyl groups specified for  $R^1$  above may be substituted, e.g. by pendant atoms or groups such as chloro, fluoro and bromo, and/or by in  
25 chain hetero atoms such as oxygen and nitrogen. Preferably, however, such hydrocarbyl groups are unsubstituted and, except in the case where  $R^1$  is an aliphatic hydrocarbyl group containing a carboxylic acid or carboxylic acid ester substituent, contain only  
30 carbon and hydrogen atoms.

The ester lubricants of Formula II may be prepared by reacting the appropriate polyol or mixture of polyols with the appropriate carboxylic acid or mixture of acids. Esterifiable derivatives of the carboxylic  
35 acids may also be used in the synthesis, such as the acyl halides, anhydrides and lower alkyl esters

thereof. Suitable acyl halides are the acyl chlorides  
and suitable lower alkyl esters are the methyl esters.  
5 Aliphatic polycarboxylic acids, or esterifiable  
derivatives thereof, may also be used in the synthesis  
of the ester lubricant. Where an aliphatic  
polycarboxylic acid is used in the synthesis of the  
ester lubricant, the resulting lubricant will comprise  
1-0 one or more compounds of Formula II in which at least  
one of the R<sup>1</sup> groups is an aliphatic hydrocarbyl group  
(linear or branched) containing a carboxylic acid or  
carboxylic acid ester substituent. The ability of  
polycarboxylic acids to react with two or more alcohol  
15 molecules provides a means of increasing the molecular  
weight of the ester formed and so a means of increasing  
the viscosity of the lubricant. Examples of such  
polycarboxylic acids include maleic acid, adipic acid  
and succinic acid, especially adipic acid. Generally,  
20 however, only monocarboxylic acids (or esterifiable  
derivatives thereof) will be used in the synthesis of  
the ester lubricant, and where polycarboxylic acids are  
used they will be used together with one or more  
monocarboxylic acids (or esterifiable derivatives  
25 thereof) and will constitute only a minor proportion of  
the total amount of carboxylic acids used in the  
synthesis. Where an aliphatic polycarboxylic acid (or  
an esterifiable derivative thereof) is employed in the  
synthesis, it will preferably constitute no more than  
30 mole %, more preferably no more than 10 mole % of  
the total amount of carboxylic acids used in the  
synthesis, with one or more monocarboxylic acids (or  
esterifiable derivatives thereof) constituting the  
remainder.

35 Usually, the amount of the carboxylic acid(s) (or  
esterifiable derivative thereof) which is used in the

5 synthesis will be sufficient to esterify all of the  
hydroxyl groups contained in the polyol(s), in which  
case the resulting lubricant will comprise one or more  
compounds of Formula II in which R is the hydrocarbon  
radical remaining after removing the hydroxyl groups  
from pentaerythritol, dipentaerythritol,  
tripentaerythritol, trimethylol ethane, trimethylol  
10 propane or neopentyl glycol. However, in certain  
circumstances ester lubricants which comprise residual  
hydroxyl functionality may be acceptable. Such  
lubricants comprise one or more ester compounds of  
Formula II in which R is the hydroxyl containing  
15 hydrocarbon radical remaining after removing a  
proportion of the hydroxyl groups from pentaerythritol,  
dipentaerythritol, tripentaerythritol, trimethylol  
ethane, trimethylol propane or neopentyl glycol. Esters  
containing residual (unreacted) hydroxyl functionality  
20 are often termed partial esters, and lubricants  
containing them may be prepared by utilising an amount  
of the carboxylic acid or acids which is insufficient  
to esterify all of the hydroxyl groups contained in the  
polyol or polyols.

25 It will be appreciated that the preferred  
neopentyl polyol ester lubricants may comprise a single  
compound of Formula II, i.e. the reaction product which  
is formed between a single polyol and a single  
monocarboxylic acid. However, such ester lubricants may  
30 also comprise a mixed ester composition comprising two  
or more compounds of Formula II. Such mixed ester  
compositions may be prepared by utilising two or more  
polyols and/or two or more carboxylic acids (or  
esterifiable derivatives thereof) in the synthesis of  
35 the ester, or by combining a mixture of different  
esters each of which is the reaction product of a

particular polyol and a particular carboxylic acid.  
Furthermore, different mixed ester compositions, each  
of which has been prepared by utilising two or more  
polyols and/or two or more carboxylic acids (or  
esterifiable derivatives thereof) in their synthesis,  
may also be blended together.

The preferred neopentyl polyol ester lubricants  
comprise one or more compounds of Formula II in which R  
is the hydrocarbon radical remaining after removing the  
hydroxyl groups from pentaerythritol,  
dipentaerythritol, trimethylol propane or neopentyl  
glycol. Particularly preferred alcohols for the  
synthesis of the ester are pentaerythritol,  
dipentaerythritol and trimethylol propane.

Preferably, each R<sup>1</sup> in Formula II is,  
independently, a linear aliphatic hydrocarbyl group or  
a branched aliphatic hydrocarbyl group.

Preferred linear aliphatic hydrocarbyl groups for  
R<sup>1</sup> are the linear alkyl groups, particularly the C<sub>3-10</sub>  
linear alkyl groups, more particularly the C<sub>5-10</sub> linear  
alkyl groups and especially the C<sub>5-8</sub> linear alkyl  
groups. Examples of suitable linear alkyl groups  
include n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl  
and n-decyl. Esters containing such alkyl groups can be  
prepared by utilising a linear alkanolic acid in the  
synthesis of the ester.

Preferred branched aliphatic hydrocarbyl groups  
for R<sup>1</sup> are the branched alkyl groups, particularly the  
C<sub>4-14</sub> branched alkyl groups, more particularly the  
C<sub>6-12</sub> branched alkyl groups and especially the C<sub>8-10</sub>  
branched alkyl groups. Examples of suitable branched  
alkyl groups include isopentyl, isohexyl, isoheptyl,  
isooctyl, isononyl, isodecyl, 2-ethylbutyl,  
2-methylhexyl, 2-ethylhexyl, 3,5,5-trimethylhexyl,



neopentyl, neoheptyl and neodecyl. Esters containing such alkyl groups can be prepared by utilising a branched alkanoic acid in the synthesis of the ester.

In a particularly preferred embodiment of the present invention, the ester lubricant comprises one or more esters of general formula:



wherein

15  $\text{R}^2$  is the hydrocarbon radical remaining after removing the hydroxyl groups from pentaerythritol, dipentaerythritol or trimethylol propane;

each  $\text{R}^3$  is, independently, a linear alkyl group or a branched alkyl group; and

20  $p$  is an integer of 3, 4 or 6,  
wherein one or more of the named polyols, one or more linear alkanoic acids, or esterifiable derivatives thereof, and optionally one or more branched alkanoic acids, or esterifiable derivatives thereof, are  
25 utilised in the synthesis of the ester lubricant.

Preferably, a mixture of two or more linear alkanoic acids, in particular two, or esterifiable derivatives thereof, are utilised in the synthesis of the ester. More preferably, a mixture of one or more  
30 linear alkanoic acids, or esterifiable derivatives thereof, and one or more branched alkanoic acids, or esterifiable derivatives thereof, are utilised in the synthesis. Thus, particularly preferred ester  
lubricants of the invention are mixed ester  
35 compositions which comprise a plurality of compounds of Formula III.

Where a mixture of linear and branched alkanolic acids (or esterifiable derivatives thereof) are  
5 utilised in the synthesis of the ester, as is preferred, the linear alkanolic acid(s) preferably constitutes at least 25 mole %, e.g. from 25 to 75 mole %, of the total amount of carboxylic acids used. In this way, at least 25 mole %, e.g. from 25 to 75  
10 mole %, of the hydroxyl groups contained in the polyol or mixture of polyols may be reacted with the said linear alkanolic acid(s).

Ester based lubricants comprising one or more compounds of Formula III provide a particularly good  
15 balance between the properties desired of a lubricant and, in particular, exhibit good thermal stability, good hydrolytic stability and acceptable solubility and miscibility with the heat transfer fluid. As stated previously, the present invention is particularly  
20 concerned with the provision of a working fluid composition which can replace the existing working fluid compositions comprising R-22 or R-502 as the refrigerant. Refrigeration systems which contain replacements for R-22 and R-502 typically operate at  
25 temperatures above those using R-134a as the sole replacement refrigerant. Thus, it is particularly desirable that the lubricant which is used in a working fluid composition designed to replace the existing compositions based on R-22 and R-502 exhibits good  
30 thermal stability.

Preferably,  $R^2$  is the hydrocarbon radical remaining after removing the hydroxyl groups from pentaerythritol or dipentaerythritol.

Preferred linear and branched alkyl groups for  $R^3$   
35 are those described above in connection with  $R^1$  and are

derived by utilising the corresponding alkanolic acids or esterifiable derivatives thereof.

5           An especially preferred ester based lubricant comprises a mixed ester composition which comprises a plurality of esters of Formula III and which is the reaction product of pentaerythritol, heptanoic acid and a mixture of branched C<sub>8</sub>-10 alkanolic acids. Preferably, 10 the heptanoic acid will constitute from 25 to 75 mole % of the total amount of acids utilised in the synthesis, with the branched C<sub>8</sub>-10 acids constituting the remainder. Esterifiable derivatives of the acids may also be used in the synthesis of the ester.

15           The lubricant will typically be part of a lubricant composition which also comprises one or more of the additives which are conventional in the refrigeration lubricants art. Specific mention may be made of oxidation resistance and thermal stability 20 improvers, corrosion inhibitors, metal deactivators, viscosity index improvers, anti-wear agents and extreme pressure resistance additives. Such additives are well known to those skilled in the art. Where the lubricant is part of a lubricant composition containing one or 25 more additives, such additives may be present in the amounts conventional in the art. Preferably, the cumulative weight of all the additives will not be more than 8 %, e.g. 5 %, of the total weight of the lubricant composition.

30           Suitable oxidation resistance and thermal stability improvers may be selected from the diphenyl-, dinaphthyl-, and phenylnaphthyl-amines, the phenyl and naphthyl groups of which may be substituted. Specific examples include N,N'-diphenyl phenylenediamine, 35 p-octyldiphenylamine, p,p-dioctyldiphenylamine, N-phenyl-1-naphthyl amine, N-phenyl-2-naphthyl amine,

5 N-(p-dodecyl)-phenyl-2-naphthyl amine, di-1-naphthyl  
amine, and di-2-naphthyl amine. Other suitable  
oxidation resistance and thermal stability improvers  
may be selected from the phenothiazines such as  
N-alkylphenothiazines, and the hindered phenols such as  
6-(t-butyl) phenol, 2,6-di-(t-butyl) phenol,  
4-methyl-2,6-di-(t-butyl) phenol and  
10 4,4'-methylenebis(-2,6-di-[t-butyl] phenol).

Suitable cuprous metal deactivators may be  
selected from imidazole, benzimidazole,  
2-mercaptobenzthiazole, 2,5-dimercaptothiadiazole,  
salicylidine-propylenediamine, pyrazole, benzotriazole,  
15 tolutriazole, 2-methylbenzimidazole, 3,5-dimethyl  
pyrazole, and methylene bis-benzotriazole. Examples of  
more general metal deactivators and/or corrosion  
inhibitors include organic acids and the esters, metal  
salts and anhydrides thereof, such as  
20 N-oley-l-sarcosine, sorbitan monooleate, lead  
naphthenate, dodecenyl-succinic acid and its partial  
esters and amides, and 4-nonylphenoxy acetic acid;  
primary, secondary and tertiary aliphatic and  
cycloaliphatic amines and amine salts of organic and  
25 inorganic acids, such as oil soluble alkylammonium  
carboxylates; heterocyclic nitrogen containing  
compounds, such as thiadiazoles, substituted  
imidazolines, and oxazolines; quinolines, quinones and  
anthraquinones; ester and amide derivatives of alkenyl  
30 succinic anhydrides or acids, dithiocarbamates,  
dithiophosphates; and amine salts of alkyl acid  
phosphates and their derivatives.

Suitable viscosity index improvers include  
polymethacrylate polymers, copolymers of vinyl  
pyrrolidone and methacrylates, polybutene polymers, and  
35 copolymers of styrene and acrylates.

5           Examples of suitable anti-wear and extreme  
pressure resistance agents include sulphurised fatty  
acids and fatty acid esters, such as sulphurised octyl  
tallate; sulphurised terpenes; sulphurised olefins;  
organopolysulphides; organo phosphorous derivatives  
including amine phosphates, alkyl acid phosphates,  
10       dialkyl phosphates, aminedithiophosphates, trialkyl and  
triaryl phosphorothionates, trialkyl and triaryl  
phosphines, and dialkylphosphites, e.g., amine salts of  
phosphoric acid monohexyl ester, amine salts of  
dinonylnaphthalene sulphonate, triphenyl phosphate,  
15       trinaphthyl phosphate, diphenyl cresyl and dicresyl  
phenyl phosphates, tricresyl phosphate, naphthyl  
diphenyl phosphate, triphenylphosphorothionate;  
dithiocarbamates, such as an antimony dialkyl  
dithiocarbamate; chlorinated and/or fluorinated  
hydrocarbons, and xanthates.

20           The working fluid compositions of the invention  
will typically comprise a major amount of the heat  
transfer fluid and a minor amount of the synthetic  
lubricant. Preferably, the working fluid compositions  
of the invention will comprise from 50 to 99 % by  
25       weight, more preferably from 70 to 99 % by weight, of  
the heat transfer fluid and from 1 to 50 % by weight,  
more preferably from 1 to 30 % by weight, of the  
lubricant based on the total weight thereof.

30           The working fluid compositions are useful in all  
types of compression cycle heat transfer devices. Thus,  
they may be used to provide cooling by a method  
involving condensing the heat transfer fluid and  
thereafter evaporating it in a heat exchange  
relationship with a body to be cooled. They may also  
35       be used to provide heating by a method involving  
condensing the heat transfer fluid in a heat exchange

relationship with a body to be heated and thereafter evaporating it.

5           The working fluid compositions of the invention provide a good compromise between performance and low or zero ozone depletion. They are especially suitable for applications currently satisfied by refrigerants R-22 and R-502.

10           The present invention is now illustrated, but not limited, with reference to the following Examples.

          The working fluid compositions of the invention which were investigated in the following Examples comprised a lubricant and a heat transfer fluid which  
15           was either a binary mixture of 1,1,1,2-tetrafluoroethane (R-134a) and difluoromethane (R-32) or a ternary mixture of 1,1,1,2-tetrafluoroethane (R-134a), difluoromethane (R-32) and pentafluoroethane (R-125).

          1,1,1,2-tetrafluoroethane, difluoromethane and  
20           pentafluoroethane are at least partially soluble in each of the lubricants tested which means the converse is true, i.e. each of the lubricants tested will be at least partially soluble in each of these hydrofluoroalkanes. Moreover, each lubricant tested is  
25           at least partially soluble in the binary or ternary mixtures themselves.

Example 1

30           In this Example various working fluid compositions were prepared comprising 15 % w/w of a lubricant and the complementary percentage of a heat transfer fluid comprising (by weight) equal proportions of R-134a and R-32. The lower miscibility temperature of each  
35           composition, i.e. the lowest temperature at which the lubricant remained miscible with the heat transfer

fluid, was determined. The method employed was as follows:

5           A set amount of the lubricant to be tested was placed in a previously evacuated thick walled test tube and the tube was then placed in a cooling bath regulated at the desired temperature. Once the tube was sufficiently cold, a set amount of the heat transfer  
10 fluid was condensed into the test tube. The tube was then removed from the cooling bath and the contents allowed to warm to room temperature. After the contents had been allowed to equilibrate at room temperature, they were agitated and visually examined for evidence  
15 of phase separation (the mixture looks cloudy). If there was no evidence of phase separation, the temperature of the mixture was lowered in a cooling bath at a rate of 1 °C per minute until phase separation was observed. The temperature at which phase  
20 separation was first observed was recorded as the lower miscibility temperature.

25           The results are shown in Table 1. Each lubricant is at least partially soluble in each of the components of the heat transfer fluid and also in the fluid itself.

30           The lower miscibility temperatures of a series of compositions comprising 15 % w/w of a lubricant and the complementary percentage of a single hydrofluoroalkane selected from R-134a, R-32 and R-125 were also determined. The compositions were prepared and the lower miscibility temperatures determined using the procedure described above. The results are shown in Table 1A. In Table 1A it will be noticed that the lower  
35 miscibility temperatures are in some cases quoted as being less than -60 °C. This means that at -60 °C phase separation was not observed.

TABLE 1

LUBRICANT	LOWER MISCIBILITY TEMPERATURE (°C)
PE6	-27
"EMKARATE" (TM) RL-212	-3
"EMKARATE" (TM) RL-184	>10
"EMKAROX" (TM) RL-118	I

TABLE 1A

LUBRICANT	LOWER MISCIBILITY TEMPERATURE (°C)		
	R-134a	R-32	R-125
PE6	<-60	0	<-60
"EMKARATE" (TM) RL-212	-25	>20	<-60
"EMKARATE" (TM) RL-184	10	>20	<-60
"EMKAROX" (TM) RL-118	<-60	I	<-60

I - denotes immiscibility over the temperature range -50 °C to +20 °C.

PE6 is an ester of pentaerythritol and n-hexanoic acid.

"EMKARATE" (TM) RL-212 is a commercially available ester based lubricant for use with R-134a obtainable from ICI Chemicals & Polymers Ltd. Specifically, the lubricant comprises an ester of trimethylol propane and heptanoic acid.

"EMKARATE" (TM) RL-184 is a commercially available ester based lubricant for use with R-134a obtainable from ICI Chemicals & Polymers Ltd. Specifically, the



lubricant comprises an ester of pentaerythritol,  
heptanoic acid and a mixture of branched C<sub>8-10</sub> alkanolic  
acids.

"EMKAROX" (TM) RL-118 is a commercially available  
polyoxyalkylene glycol based lubricant for use with  
R-134a obtainable from ICI Chemicals & Polymers Ltd.  
Specifically, the lubricant comprises an end-capped  
polyoxyalkylene glycol.

"EMKARATE" and "EMKAROX" are trademarks of ICI  
Chemicals & Polymers Ltd.

#### Example 2

In this Example a series of working fluid  
compositions were prepared comprising varying  
proportions of a lubricant comprising an ester of  
pentaerythritol and n-hexanoic acid and a heat transfer  
fluid comprising 70 % by weight of R-134a and 30 % by  
weight of R-32. The lubricant is at least partially  
soluble in each of the components of the heat transfer  
fluid and also in the fluid itself. The lower  
miscibility temperature of each composition was  
determined. The compositions were prepared and the  
lower miscibility temperatures determined using the  
procedure described in Example 1.

The results are shown in Table 2. In Table 2 it  
will be noticed that the lower miscibility temperature  
of one of the compositions is quoted as being less than  
-50 °C. This means that at -50 °C phase separation was  
not observed.

TABLE 2

Working fluid composition		Lower miscibility temperature (°C)
% by weight of lubricant	% by weight of heat transfer fluid	
10.8	89.2	-30
20.3	79.7	-25
27.5	72.5	-32
36.9	63.1	-38
46.0	54.0	-47
68.0	32.0	< -50

Example 3

In this Example a series of working fluid compositions were prepared comprising varying proportions of a lubricant and a heat transfer fluid comprising 70 % by weight of R-134a and 30 % by weight of R-32. The lubricant comprised an ester of dipentaerythritol, n-hexanoic acid and a branched C<sub>6</sub> carboxylic acid, i.e. a branched acid comprising 6 carbon atoms, and is at least partially soluble in each of the components of the heat transfer fluid and also in the fluid itself. The lower miscibility temperature of each composition was again determined. The compositions were prepared and the lower miscibility temperatures determined using the procedure described in Example 1.

The results are shown in Table 3. In Table 3 it will be noticed that the lower miscibility temperature of one of the compositions is quoted as being less than

-55 °C. This means that at -55 °C phase separation was not observed.

TABLE 3

Working fluid composition		Lower miscibility temperature (°C)
Z by weight of lubricant	Z by weight of heat transfer fluid	
10.0	90.0	-32
17.3	82.7	-28
38.0	62.0	-35
46.2	53.8	-41
57.8	42.2	Slightly immiscible at -55
68.8	31.2	< -55

Example 4

In this Example a series of working fluid compositions were prepared comprising varying proportions of a lubricant and a heat transfer fluid comprising 70 Z by weight of R-134a and 30 Z by weight of R-32. The lubricant comprised a mixture of the lubricants used in Examples 2 and 3, i.e. a mixture comprising an ester of pentaerythritol and n-hexanoic acid and an ester of dipentaerythritol, n-hexanoic acid and a branched C<sub>6</sub> carboxylic acid, and is at least partially soluble in each of the components of the heat transfer fluid and also in the fluid itself. The lower miscibility temperature of each composition was again determined. The compositions were prepared and the

lower miscibility temperatures determined using the procedure described in Example 1.

The results are shown in Table 4. In Table 4 it will be noticed that the lower miscibility temperature of one of the compositions is quoted as being less than -50 °C. This means that at -50 °C phase separation was not observed.

TABLE 4

10280

Working fluid composition		Lower miscibility temperature (°C)
% by weight of lubricant	% by weight of heat transfer fluid	
10.5	89.5	-31
19.7	80.3	-27
28.9	71.1	-29
41.1	58.9	-32
48.0	52.0	-39
55.2	44.8	-46
69.7	30.3	< -50

Example 5

In this Example a series of working fluid compositions were prepared comprising varying proportions of a lubricant comprising an ester of pentaerythritol and n-hexanoic acid and a heat transfer fluid comprising 50 % by weight of R-134a, 30 % by weight of R-32 and 20 % by weight of R-125. The lubricant is at least partially soluble in each of the components of the heat transfer fluid and also in the fluid itself. The lower miscibility temperature of each composition was again determined. The compositions were

prepared and the lower miscibility temperatures determined using the procedure described in Example 1.

The results are shown in Table 5. In Table 5 it will be noticed that the lower miscibility temperature of some of the compositions is quoted as being less than -50 °C. This means that at -50 °C phase separation was not observed.

TABLE 5

Working fluid composition		Lower miscibility temperature (°C)
Z by weight of lubricant	Z by weight of heat transfer fluid	
10.2	89.8	< -50
22.0	78.0	-48
29.7	70.3	< -50
41.6	58.4	< -50
48.6	51.4	< -50
60.7	39.3	< -50

It will be appreciated that the binary mixtures of R-134a and R-32 and the ternary mixtures of R-134a, R-32 and R-125 which form the subject of the above Examples can also be used in combination with other neopentyl polyol ester type lubricants to yield viable working fluid compositions. Moreover, binary mixtures of R-134a and R-32 and ternary mixtures of R-134a, R-32 and R-125 comprising different proportions of the constituent hydrofluoroalkanes to the mixtures exemplified above can also be used in combination with neopentyl polyol ester type lubricants to yield viable working fluid compositions.